

## PATENT ABSTRACTS OF JAPAN

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(71)Applicant : TOYOTA CENTRAL RES & DEV LAB  
INC

TOYOTA MOTOR CORP

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(72)Inventor : TAKESHITA TOMOHIRO

MIURA FUSAYOSHI

MORIMOTO TOMO

KOBAYASHI MASAFUMI

KATO MANABU

TAKEUCHI NORIMITSU

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(54) ELECTROLYTE MEMBRANE ELECTRODE JOINT BODY FOR SOLID POLYMER TYPE FUEL CELL AND SOLID POLYMER TYPE FUEL CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an electrolyte membrane electrode joint body for a solid polymer type fuel cell capable of efficiently decomposing peroxide produced in the cell and having high deterioration suppressing effect for an electrode and an electrolyte membrane.

SOLUTION: This electrolyte membrane electrode joint body for a solid polymer type fuel cell is composed by providing the electrolyte membrane having ion conductivity and a pair of electrodes formed on both sides of the electrolyte membrane; and a peroxide decomposing catalyst for decomposing the peroxide is disposed on at least either of the pair of electrodes with a concentration difference.

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### LEGAL STATUS

[Date of request for examination]

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**CLAIMS**

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[Claim(s)]

[Claim 1]

It has the electrolyte membrane which has ion conductivity, and the electrode of the couple prepared in the both sides of this electrolyte membrane,

The electrolyte membrane electrode zygote for polymer electrolyte fuel cells characterized by arranging the peroxide decomposition catalyst which disassembles a peroxide at least into one side of the electrode of said couple with a concentration difference.

[Claim 2]

Said peroxide decomposition catalyst is an electrolyte membrane electrode zygote for polymer electrolyte fuel cells according to claim 1 arranged by having a concentration difference in the thickness direction of said electrode.

[Claim 3]

Said peroxide decomposition catalyst is an electrolyte membrane electrode zygote for polymer electrolyte fuel cells according to claim 2 arranged so that a concentration value may increase toward said electrolyte membrane side.

[Claim 4]

The concentration of this peroxide decomposition catalyst in near the interface of said electrolyte membrane and the electrode with which said peroxide decomposition catalyst has been arranged is an electrolyte membrane electrode zygote for polymer electrolyte fuel cells according to claim 3 which is less than [ more than 1wt%8wt% ].

[Claim 5]

the fuel electrode with which the fuel gas with which the electrode of said couple contains hydrogen is supplied, and the oxygen pole to which the oxidant gas containing oxygen is supplied -- since  
The electrolyte membrane electrode zygote for polymer electrolyte fuel cells according to claim 1 with which said peroxide decomposition catalyst is arranged on this oxygen pole.

[Claim 6]

Said peroxide decomposition catalyst is an electrolyte membrane electrode zygote for polymer electrolyte fuel cells according to claim 1 which is more than a kind chosen from a metal, a metallic oxide, metallic phosphate, a metal fluoride, and a large annular metal complex.

[Claim 7]

Said peroxide decomposition catalyst is an electrolyte membrane electrode zygote for polymer electrolyte fuel cells according to claim 1 which is more than a kind chosen from Ru, Ag, RuO<sub>2</sub>, WO<sub>3</sub>, CeO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>, CePO<sub>4</sub>, CrPO<sub>4</sub>, AlPO<sub>4</sub>, FePO<sub>4</sub>, CeF<sub>3</sub> and FeF<sub>3</sub>, Fe-porphyrin, Co-porphyrin, a hem, and a catalase.

[Claim 8]

The polymer electrolyte fuel cell equipped with the electrolyte membrane electrode zygote for polymer electrolyte fuel cells according to claim 1.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[Field of the Invention]

[0001]

Especially this invention relates to the electrolyte membrane electrode zygote used for a polymer electrolyte fuel cell about a polymer electrolyte fuel cell.

[Background of the Invention]

[0002]

Generation efficiency is high, the fuel cell which generates the electrical and electric equipment according to the electrochemical reaction of gas has clean gas discharged, and there is very little effect to an environment. Therefore, various applications, such as an object for a generation of electrical energy and a power source for automobiles of low pollution, are expected in recent years.

[0003]

Especially, a polymer electrolyte fuel cell can be operated at about 80-degree C low temperature, and has big output density. A polymer electrolyte fuel cell usually uses a poly membrane with proton conductivity as an electrolyte. The electrode of a couple which turns into a fuel electrode and an oxygen pole, respectively is prepared in the both sides of the poly membrane (electrolyte membrane) used as an electrolyte, and an electrolyte membrane electrode zygote (MEA) is constituted. The single cel which pinched this electrolyte membrane electrode zygote with the separator serves as a generation-of-electrical-energy unit. And fuel gas, such as hydrogen and a hydrocarbon, is supplied to a fuel electrode, oxidant gas, such as oxygen and air, is supplied to an oxygen pole, respectively, and it generates electricity according to the electrochemical reaction in the three-phase zone of gas, an electrolyte, and an electrode.

[0004]

However, a polymer electrolyte fuel cell has the problem that the cell engine performance will fall, by prolonged operation. As a cause of cell performance degradation, degradation of an electrolyte membrane and an electrode is cited, for example. At the time of operation of a polymer electrolyte fuel cell, water is generated from hydrogen and oxygen on an oxygen pole. However, reduction of the oxygen in an oxygen pole stops at 2 electronic reactions, and a hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) may be generated by the service condition etc. The generated hydrogen peroxide is understood by the radical under existence of a metal ion etc. It is thought that an electrolyte membrane and an electrode receive breakage and deteriorate by the hydrogen-peroxide radical.

[0005]

Moreover, many of electrolyte membranes are poly membranes which consist of a hydrocarbon system ingredient or a fluorine system ingredient. It has been thought that a fluorine system electrolyte membrane hardly receives breakage with peroxides, such as a hydrogen peroxide, conventionally. However, as a result of repeating examination variously, even if it was a fluorine system electrolyte membrane, it turned out that a peroxide may receive breakage. In this case, since C-F association is decomposed by the peroxide, there is a problem which fluoric acid etc. produces.

[0006]

Degradation of the electrolyte membrane by the peroxide etc. is controlled and making an electrolyte membrane and an electrode contain metals, such as a ruthenium, manganese, and cobalt, or those oxides is proposed as an attempt which raises the endurance of a fuel cell (for example, the patent reference 1, 2 reference.).

[Patent reference 1] JP,2001-118591,A

[Patent reference 2] JP,2003-123777,A

## [Description of the Invention]

## [Problem(s) to be Solved by the Invention]

[0007]

However, by the technique shown in the above-mentioned patent reference 1 and 2, a metal with them is used. [ there are few amounts of resources and expensive as the metal made to contain and its oxide, ] Therefore, there is a problem in utilization in reservation of a resource, and the field of cost. Moreover, when the content of the above-mentioned metal or an oxide is made to increase in order to raise the decomposition effectiveness of a peroxide, there is also a problem that a cell reaction will be checked. At the time of operation of a polymer electrolyte fuel cell, the interior of a cell serves as harsh environments, such as an acid ambient atmosphere, under an about 80-degree C elevated temperature further again. The metal and oxide which were made to contain tend to be eluted under such hot and acid conditions. So, it is difficult to make the decomposition effectiveness of a peroxide maintain.

[0008]

This invention is made in view of such the actual condition, and it makes it a technical problem to offer the electrolyte membrane electrode zygote for polymer electrolyte fuel cells which can disassemble efficiently peroxides, such as a hydrogen peroxide generated within the cell, without using so much the peroxide decomposition catalyst which disassembles a peroxide. Moreover, even when you operate by using the electrolyte membrane electrode zygote for a long period of time, let it be a technical problem to offer the polymer electrolyte fuel cell with which the cell engine performance cannot fall easily.

## [Means for Solving the Problem]

[0009]

The electrolyte membrane electrode zygote for polymer electrolyte fuel cells of this invention is equipped with the electrolyte membrane which has ion conductivity, and the electrode of the couple prepared in the both sides of this electrolyte membrane, and is characterized by arranging the peroxide decomposition catalyst which disassembles a peroxide at least into one side of the electrode of said couple with a concentration difference.

[0010]

In the electrolyte membrane electrode zygote of this invention, the electrode of a couple which turns into a fuel electrode and an oxygen pole at the both sides of an electrolyte membrane, respectively is arranged. A peroxide decomposition catalyst is included in either [ at least ] this fuel electrode or an oxygen pole.

[0011]

In an electrode, a peroxide decomposition catalyst is arranged with a concentration difference. Here, in an electrode, the concentration of a peroxide decomposition catalyst is not so fixed as "having a concentration difference", and it means that the concentration of an oxide decomposition catalyst changes with fields of an electrode. There may be a concentration difference in the thickness direction of an electrode, and there may be in the direction of a field of an electrode.

[0012]

For example, in the field expected that many peroxides generate, a peroxide decomposition catalyst is arranged so that the concentration may become high, and in the field which is not so, it is arranged to it so that the concentration may become low. Thus, by arranging, a peroxide can be disassembled effectively, without increasing the quantity of a peroxide decomposition catalyst. Moreover, if a peroxide decomposition catalyst is arranged near the interface of an electrolyte membrane and an electrode so that the concentration may become high, the diffusion to the electrolyte membrane of the generated peroxide can be controlled effectively.

[0013]

Thus, in the electrolyte membrane electrode zygote of this invention, by adjusting concentration distribution of the peroxide decomposition catalyst arranged at an electrode, generation of a peroxide and a diffusion condition can be embraced, and a peroxide can be disassembled and defanged efficiently. So, even if peroxide \*\*\*\*\* to be used is little, the degradation depressor effect of an electrode and an electrolyte membrane is high. Moreover, since the electrolyte membrane electrode zygote of this invention can disassemble a peroxide efficiently with a small amount of peroxide decomposition catalyst, it is practical also in respect of cost.

[0014]

The polymer electrolyte fuel cell of this invention is characterized by having the electrolyte membrane electrode zygote of above-mentioned this invention. That is, in the polymer electrolyte fuel cell of this invention, even if a peroxide generates at the time of operation, a peroxide is promptly disassembled by the

peroxide decomposition catalyst. Therefore, there is little degradation of the electrolyte membrane at the time of operation and an electrode, and even when it operates for a long period of time, there is little cell performance degradation.

[Effect of the Invention]

[0015]

In the electrolyte membrane electrode zygote for polymer electrolyte fuel cells of this invention, the peroxide decomposition catalyst which disassembles a peroxide at least into one side of the electrode of a couple is arranged with a concentration difference. Therefore, generation of a peroxide and a diffusion condition can be embraced, and a peroxide can be disassembled and defanged efficiently. Therefore, even when there is little degradation of an electrode and an electrolyte membrane and it operates for a long period of time in the polymer electrolyte fuel cell equipped with the electrolyte membrane electrode zygote of this invention, there is little cell performance degradation.

[Best Mode of Carrying Out the Invention]

[0016]

Below, the operation gestalt of the electrolyte membrane electrode zygote for polymer electrolyte fuel cells of this invention and a polymer electrolyte fuel cell is explained. In addition, the electrolyte membrane electrode zygote for polymer electrolyte fuel cells and polymer electrolyte fuel cell of this invention are not limited to the following operation gestalt. The electrolyte membrane electrode zygote for polymer electrolyte fuel cells and polymer electrolyte fuel cell of this invention can be carried out with the various gestalten which performed modification which this contractor can make, amelioration, etc. in the range which does not deviate from the summary of this invention.

[0017]

<The electrolyte membrane electrode zygote for polymer electrolyte fuel cells>

The electrolyte membrane electrode zygote of this invention is equipped with the electrolyte membrane which has ion conductivity, and the electrode of the couple prepared in the both sides of this electrolyte membrane, and the peroxide decomposition catalyst which disassembles a peroxide at least into one side of the electrode of said couple is arranged with a concentration difference.

[0018]

Generally, the electrode, i.e., the fuel electrode, and oxygen pole of a couple consist of a catalyst bed and a diffusion layer, respectively. A catalyst bed is the reaction field of electrochemical reaction, and contains an electrode catalyst and polyelectrolytes, such as platinum supported by carbon. A diffusion layer plays the role which delivers and receives an electron between catalyst beds, and serves as supply of the reactant gas to a catalyst bed from porous materials, such as a carbon cross. The catalyst bed of each electrode is formed in both the front faces of an electrolyte membrane, respectively, and the laminating of the diffusion layer is carried out to the front face of each catalyst bed.

[0019]

In this case, as for a peroxide decomposition catalyst, being arranged at the catalyst bed which constitutes an electrode is desirable. Diffusion of the peroxide to the electrolyte membrane which adjoins by arranging a peroxide decomposition catalyst to a catalyst bed in addition to the ability to disassemble the generated peroxide promptly can also be controlled effectively.

[0020]

Moreover, the peroxide decomposition catalyst may be arranged at either the fuel electrode and the oxygen pole, or may be arranged at both. It is desirable to arrange a peroxide decomposition catalyst from a viewpoint of disassembling promptly the peroxide generated especially, to the oxygen pole.

[0021]

A peroxide decomposition catalyst is arranged with a concentration difference in an electrode. There may be a concentration difference in the thickness direction of an electrode, and there may be in the direction of a field of an electrode. Especially how to attach a concentration difference is not limited and should just adjust suitably according to generation of a peroxide, and a diffusion condition. For example, in the thickness direction or the direction of a field of an electrode, a concentration difference may be given stair-like and a concentration gradient in which concentration carries out abbreviation per-continuum change may be given so that concentration may change gradually. Moreover, a concentration difference with other fields which arrange a peroxide decomposition catalyst only to a certain field, and do not arrange a peroxide decomposition catalyst may be given.

[0022]

It is desirable to arrange a peroxide decomposition catalyst with a concentration difference especially in the

thickness direction of an electrode. In this case, the mode which a concentration value increases toward an electrolyte membrane side is more desirable. By arranging many peroxide decomposition catalysts to the electrolyte membrane side of an electrode, diffusion of the peroxide to an electrolyte membrane can be controlled more effectively.

[0023]

Moreover, in the above-mentioned mode, although the concentration of the peroxide decomposition catalyst in near the interface of an electrolyte membrane and an electrode is based also on the class of peroxide decomposition catalyst, and extent of humidification of gas supplied, it is desirable that it is more than 1wt%. It is because the decomposition effectiveness of a peroxide and the diffusion depressor effect to an electrolyte membrane are small in the case of below 1wt%. It is more suitable in it being more than 3wt%. On the other hand, when the effect on the electrochemical reaction in an electrode is taken into consideration, as for the concentration of a peroxide decomposition catalyst, it is desirable that it is less than [ 8wt% ]. It is more suitable in it being less than [ 5wt% ]. The concentration value of these peroxides decomposition catalyst is the weight rate of the peroxide decomposition catalyst at the time of making the whole catalyst bed weight into 100wt(s)%, when the peroxide decomposition catalyst has been arranged to the catalyst bed of an electrode.

[0024]

The existence of the concentration difference of the peroxide decomposition catalyst in an electrode can be checked by measuring an electrode by SIMS (secondary-ion-mass-spectroscopy equipment), or measuring an electrode cross section by EPMA (the electron ray micro analysis method).

[0025]

A peroxide decomposition catalyst will not be especially limited, if it has the catalysis which disassembles a peroxide. For example, a metal, a metallic oxide, metallic phosphate, a metal fluoride, a large annular metal complex, etc. are mentioned. What is necessary is to use independently a kind chosen from these, or just to use two or more sorts together. If it considers as a metal, as a metallic oxide, it is especially, suitable [ Fe-porphyrin, Co-porphyrin a hem, a catalase, etc. ] for Ru, Ag, etc. as CeF<sub>3</sub>, FeF<sub>3</sub> grade, and a large annular metal complex as CePO<sub>4</sub>, CrPO<sub>4</sub>, AlPO<sub>4</sub>, FePO<sub>4</sub> grade, and a metal fluoride as RuO<sub>2</sub>, WO<sub>3</sub>, CeO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub> grade, and metallic phosphate. Since it says especially that the resolvability ability of a peroxide is high, it is good to use RuO<sub>2</sub> and CePO<sub>4</sub>.

[0026]

Although especially the production approach of the electrolyte membrane electrode zygote of this invention is not limited, it is producible simple by the following approaches, for example.

[0027]

A primary method is the approach of mixing a peroxide decomposition catalyst in the catalyst ink for forming a catalyst bed. First, a peroxide decomposition catalyst is suitably mixed in the catalyst ink which made solvents, such as water and alcohol, distribute an electrode catalyst and a polyelectrolyte, and the various catalyst ink in which the concentration of a peroxide decomposition catalyst differs is prepared. Subsequently, two coats of the prepared various catalyst ink is given on the surface of an electrolyte membrane with a doctor blade method, a spray method, a spin coat method, etc., and the catalyst bed from which peroxide decomposition catalyst concentration differs in the thickness direction is formed in an electrolyte membrane front face.

[0028]

Moreover, two coats of the various catalyst ink which carried out [ above-mentioned ] preparation is given on the front face of the sheet made from PTFE, and the catalyst bed from which peroxide decomposition catalyst concentration differs in the thickness direction is formed in this sheet front face. Subsequently, the catalyst bed formed in the sheet front face is stuck by pressure with a hotpress etc. on the surface of an electrolyte membrane. A sheet is exfoliated after sticking by pressure and the catalyst bed from which peroxide decomposition catalyst concentration differs in the thickness direction is formed in an electrolyte membrane front face.

[0029]

The second approach is the approach of mixing a peroxide decomposition catalyst to the powder for catalyst bed formation. First, a peroxide decomposition catalyst is suitably mixed to the powder for catalyst bed formation which consists of an electrode catalyst and a polyelectrolyte, and the various powder for catalyst bed formation with which the concentration of a peroxide decomposition catalyst differs is prepared. Subsequently, the electrostatic-spraying cloth of the prepared various powder for catalyst bed formation is carried out to a metal base material one by one, or it carries out sequential adhesion by corona discharge

etc., and the catalyst bed from which peroxide decomposition catalyst concentration differs in the thickness direction is formed in a metal support surface. Subsequently, the catalyst bed formed in the metal support surface is stuck by pressure with a hotpress etc. on the surface of an electrolyte membrane. A metal base material is exfoliated after sticking by pressure, and the catalyst bed from which peroxide decomposition catalyst concentration differs in the thickness direction is formed in an electrolyte membrane front face.

[0030]

The third approach is the approach of arranging a peroxide decomposition catalyst to the catalyst bed of an electrode by hydrolysis processing, wet energization processing, the spatter, CVD (chemical-vapor-deposition method), etc. For example, as a peroxide decomposition catalyst, when using a metallic oxide, metallic phosphate, and a metal fluoride, by hydrolysis processing, the metal salt water solution which dissolved the salt of the metal which constitutes a peroxide decomposition catalyst in water is first contacted to a catalyst bed. Subsequently, what is necessary is to contact an acid solution to the catalyst bed, and just to hydrolyze. In addition, a nitrate, a sulfate, a chloride, etc. are suitable for a metal salt as a salt with the high solubility to water. Moreover, as a peroxide decomposition catalyst, when using a metal, the metal salt water solution which dissolved the salt of this metal in water is contacted to a catalyst bed. And what is necessary is to contact reducing agents, such as a hydrogen peroxide, a hydrazine, vitamin C, and sucrose, to the catalyst bed, and just to return to a metal.

[0031]

What is necessary is just to deposit a peroxide decomposition catalyst on this precursor front face in wet energization processing by energizing in the predetermined solution containing the salt of the metal which constitutes a peroxide decomposition catalyst for the electrolyte membrane electrode zygote precursor with which the catalyst bed was formed on the surface of the electrolyte membrane as at least one side of the electrode for electrolysis.

[0032]

What is necessary is to stick the carbon cross used as a diffusion layer etc. to the front face of the catalyst bed of each of two poles by pressure with a hotpress etc., and just to let it be an electrolyte membrane electrode zygote, after forming a catalyst bed including a peroxide decomposition catalyst on the surface of an electrolyte membrane by the approach explained above.

[0033]

In addition, especially the class of electrolyte membrane is not limited in the electrolyte membrane electrode zygote of this invention. For example, all fluorine system sulfonic-acid film, all fluorine system phosphonic acid film, all fluorine system carboxylic-acid film, the fluorine-containing hydrocarbon system graft film, the total hydrocarbon system graft film, all aromatic series film, etc. can be used. Moreover, the compound poly membrane including reinforcing materials, such as PTFE and polyimide, which strengthened the mechanical property may be used. When endurance etc. is especially taken into consideration, it is desirable to use the poly membrane of all fluorine systems. Since it says that the engine performance as an electrolyte is high especially, it is desirable to use all fluorine system sulfonic-acid film. As an example of all fluorine system sulfonic-acid film, "Nafion" (a trademark, Du Pont make), "ASHIPU REXX" (a trademark, Asahi Chemical Co., Ltd. make), the "deflection myon" (a trademark, Asahi Glass Co., Ltd. make), etc. are mentioned.

[0034]

<Polymer electrolyte fuel cell>

The polymer electrolyte fuel cell of this invention is equipped with the electrolyte membrane electrode zygote of above-mentioned this invention. For example, what is necessary is to carry out the laminating of two or more electrolyte membrane electrode zygotes of this invention through a separator, and just to constitute them. What is necessary is for the current collection engine performance to be high and just to use what covered noble metals and a carbon material also with the bottom of an oxidization steam ambient atmosphere on comparatively stable baking carbon, shaping carbon, and the front face of a stainless steel ingredient as a separator which pinches an electrolyte membrane electrode zygote.

[Example]

[0035]

Based on the above-mentioned operation gestalt, the peroxide decomposition catalyst has been arranged so that it may have a concentration difference in the thickness direction at the catalyst bed of an electrode, and the electrolyte membrane electrode zygote was produced. The cell reaction was performed using the produced electrolyte membrane electrode zygote, and extent of degradation of an electrolyte membrane and an electrode was investigated. Hereafter, it explains in order of.



[0036]

<Production of an electrolyte membrane electrode zygote>

(1) The electrolyte membrane electrode zygote of an example 1

The electrolyte membrane electrode zygote ("MEA" is called suitably hereafter.) was produced using  $\text{CePO}_4$  as a peroxide decomposition catalyst. First, the catalyst ink which does not contain  $\text{CePO}_4$  was prepared. Distilled water, ethanol, propylene glycol, and the Nafion solution (22wt% and Du Pont make) were added to the platinum catalyst (a Pt/C catalyst, rate of platinum support 60wt%) supported by carbon, and it mixed with the ultrasonic homogenizer, and considered as catalyst ink. Subsequently, the prepared catalyst ink was applied to the sheet front face made from Teflon (it is the same a trademark, the Du Pont make, and the following.) with the doctor blade method. Then, it was made to dry at a room temperature, the solvent was removed, and the peroxide decomposition catalyst non-containing layer which does not include a peroxide decomposition catalyst was formed in the sheet front face. The thickness of a peroxide decomposition catalyst a non-containing layer was about 10 micrometers.

[0037]

Next,  $\text{CePO}_4$  powder of the specified quantity was mixed in the above-mentioned catalyst ink, and three kinds of catalyst ink in which  $\text{CePO}_4$  concentration becomes 5wt% 3wt% 1wt% was prepared. Spray-applied to the front face of the above-mentioned peroxide decomposition catalyst non-containing layer, order with  $\text{CePO}_4$  low concentration was made to dry these three kinds of catalyst ink on it, and the peroxide decomposition catalyst content layer from which  $\text{CePO}_4$  concentration differs was formed in the thickness direction. Spreading of catalyst ink was performed every 5 times per each concentration, and it carried out a total of 15 times. The thickness of a peroxide decomposition catalyst content layer was about 10 micrometers.

[0038]

The hotpress of the above-mentioned sheet with which the peroxide decomposition catalyst non-containing layer, and the peroxide decomposition catalyst content layer were formed was carried out to one front face of an electrolyte membrane (it is the same a trade name "Nafion", a trademark, the Du Pont make, 50 micrometers of thickness, and the following.) at about 4.9 pressure MPa(s) and the temperature of about 120 degrees C. Then, only the sheet was exfoliated and the catalyst bed which the concentration value of  $\text{CePO}_4$  increases toward an electrolyte membrane side was formed on the surface of the electrolyte membrane. The zygote of this electrolyte membrane and catalyst bed was set to MEA of an example 1. In addition, in MEA of this example 1, a catalyst bed consists of peroxide decomposition catalyst a non-containing layer, and a peroxide decomposition catalyst content layer.

[0039]

(2) The electrolyte membrane electrode zygote of an example 2

MEA was produced using  $\text{RuO}_2$  as a peroxide decomposition catalyst. First, the catalyst ink which does not contain  $\text{RuO}_2$  was prepared like production of MEA of an example 1. The prepared catalyst ink was applied to the sheet front face made from Teflon, it dried, and the peroxide decomposition catalyst non-containing layer which does not include a peroxide decomposition catalyst was formed in the sheet front face. The thickness of a peroxide decomposition catalyst a non-containing layer was about 10 micrometers.

[0040]

Next, Ru complex ( $\text{Ru}_3(\text{NO})(\text{NO}_3)$ ) water solution (0.05wt(s)% as Ru) was dropped at the front face of a peroxide decomposition catalyst a non-containing layer. Then, it hydrolyzed in the phosphoric-acid water solution of 0.1M, and distilled water washed. From this, the catalyst bed to which  $\text{RuO}_2$  was fixed near the front face of a peroxide decomposition catalyst a non-containing layer was formed in the sheet front face.

[0041]

The hotpress of the sheet with which this catalyst bed was formed was carried out to one front face of an electrolyte membrane at about 4.9 pressure MPa(s) and the temperature of about 120 degrees C. Then, only the sheet was exfoliated and the catalyst bed containing  $\text{RuO}_2$  was formed near the interface with an electrolyte membrane on the surface of the electrolyte membrane. The zygote of this electrolyte membrane and catalyst bed was set to MEA of an example 2. In addition, when the cross section of a catalyst bed was measured by EPMA, it was checked that  $\text{RuO}_2$  is being fixed near the interface of a catalyst bed and an electrolyte membrane.

[0042]

(3) The electrolyte membrane electrode zygote of the example of a comparison

The catalyst bed was formed using the catalyst ink ( $\text{CePO}_4$  concentration: 3wt%) prepared by production of MEA of an example 1. Namely,  $\text{CePO}_4$  concentration spray-applied to the sheet front face made from



Teflon, made it dry the catalyst ink which is 3wt(s)%, and formed the catalyst bed with  $\text{CePO}_4$  fixed concentration in the thickness direction. Spreading of catalyst ink was performed 15 times and  $\text{CePO}_4$  amount added by the whole catalyst bed was made the same as MEA of an example 1. The thickness of the formed catalyst bed was about 10 micrometers.

[0043]

The hotpress of the above-mentioned sheet with which the catalyst bed was formed was carried out to one front face of an electrolyte membrane at about 4.9 pressure MPa(s) and the temperature of about 120 degrees C. Then, only the sheet was exfoliated and the catalyst bed in which  $\text{CePO}_4$  is contained by fixed concentration on the surface of an electrolyte membrane was formed. The zygote of this electrolyte membrane and catalyst bed was set to MEA of the example of a comparison.

[0044]

<Degradation examination of an electrolyte membrane etc.>

Each produced MEA was included in the cel for durability tests. That is, the separator made from carbon with which the gas passageway was formed in the both sides of MEA has been arranged, and it was held with the base material made from SUS. And the hydrogen which humidified the air humidified to the electrode (oxygen pole) of the direction in which the catalyst bed was formed to the electrode (fuel electrode) of another side was supplied, respectively, and was operated for 24 hours. The operating temperature of 100 ml/min and a cel made humidification temperature of air and hydrogen 90 degrees C, and the flow rate made it 90 degrees C.

[0045]

During cel actuation, the water discharged from the oxygen pole and the fuel electrode was collected. The fluoride ion ( $\text{F}^-$ ) concentration in recycled water was measured in ion chromatography equipment PIA-1000 (Shimadzu Make), and it asked for the fluoride ion rate of dissolution ( $\mu\text{g}/(\text{cm}^2, \text{hr})$ ). Fluoride ion rates of dissolution are unit time amount and the amount of fluoride ion eluted in per unit electrode surface product, and are computed from the amount of the recycled water from each electrode, and the fluoride ion concentration in recycled water. A fluoride ion rate of dissolution serves as an index which shows extent of degradation of an electrolyte membrane and an electrode. That is, it is shown that degradation of an electrolyte membrane etc. is advancing, so that a fluoride ion rate of dissolution is large.

[0046]

The measurement result of each fluoride ion rate of dissolution in MEA is shown in drawing 1. As shown in drawing 1, in MEA of the examples 1 and 2 which have the concentration difference of a peroxide decomposition catalyst in a catalyst bed, the fluoride ion rate of dissolution became small  $0.1 \mu\text{g}/(\text{cm}^2, \text{hr})$  following. On the other hand, in MEA of the example of a comparison without the concentration difference of a peroxide decomposition catalyst, the fluoride ion rate of dissolution became large with  $0.15 \mu\text{g}/(\text{cm}^2, \text{hr})$ . When MEA of an example 1 is especially compared with MEA of the example of a comparison, even if it uses the same quantity of a peroxide decomposition catalyst, it turns out that the MEA of the example 1 which has given and arranged the concentration difference of degradation depressor effect, such as an electrolyte membrane, is higher. Moreover, like MEA of an example 2, when a peroxide decomposition catalyst is arranged near the interface of an electrode and an electrolyte membrane, it is understood that degradation depressor effect, such as an electrolyte membrane, is high.

[0047]

As mentioned above, in MEA of this invention by which the peroxide decomposition catalyst has been arranged with a concentration difference at the electrode, it has checked that degradation of an electrolyte membrane and an electrode could not advance easily. Therefore, if MEA of this invention is used, even when it operates for a long period of time, a polymer electrolyte fuel cell with little cell performance degradation can be realized economically.

[Brief Description of the Drawings]

[0048]

[Drawing 1] The measurement result of the fluoride ion rate of dissolution in MEA of examples 1 and 2 and the example of a comparison is shown.

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[Translation done.]

\* NOTICES \*

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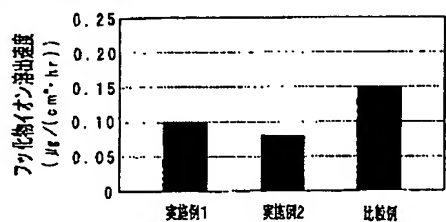
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DRAWINGS

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[Drawing 1]



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[Translation done.]

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(71) 出願人 000003609

株式会社豊田中央研究所

愛知県愛知郡長久手町大字長湫字横道4 1  
番地の1

(71) 出願人 000003207

トヨタ自動車株式会社

愛知県豊田市トヨタ町1番地

(74) 代理人 100081776

弁理士 大川 宏

(72) 発明者 竹下 朋洋

愛知県愛知郡長久手町大字長湫字横道4 1  
番地の1 株式会社豊田中央研究所内

(72) 発明者 三浦 房美

愛知県愛知郡長久手町大字長湫字横道4 1  
番地の1 株式会社豊田中央研究所内

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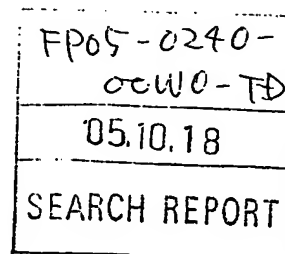
(54) 【発明の名称】 固体高分子型燃料電池用電解質膜電極接合体および固体高分子型燃料電池

(57) 【要約】

【課題】 電池内で生成された過酸化物を効率よく分解し、電極および電解質膜の劣化抑制効果が高い固体高分子型燃料電池用電解質膜電極接合体を提供する。

【解決手段】 固体高分子型燃料電池用電解質膜電極接合体を、イオン導電性を有する電解質膜と、該電解質膜の両側に設けられた一対の電極と、を備えて構成し、該一対の電極の少なくとも一方に、過酸化物を分解する過酸化物分解触媒を濃度差をつけて配置する。

【選択図】 なし



## 【特許請求の範囲】

## 【請求項 1】

イオン導電性を有する電解質膜と、該電解質膜の両側に設けられた一対の電極と、を備え、

前記一対の電極の少なくとも一方に、過酸化物を分解する過酸化物分解触媒が濃度差をもって配置されることを特徴とする固体高分子型燃料電池用電解質膜電極接合体。

## 【請求項 2】

前記過酸化物分解触媒は、前記電極の厚さ方向に濃度差をもって配置される請求項 1 に記載の固体高分子型燃料電池用電解質膜電極接合体。

## 【請求項 3】

前記過酸化物分解触媒は、前記電解質膜側に向かって濃度値が増加するように配置される請求項 2 に記載の固体高分子型燃料電池用電解質膜電極接合体。

## 【請求項 4】

前記電解質膜と前記過酸化物分解触媒が配置された電極との界面付近における該過酸化物分解触媒の濃度は、1 wt % 以上 8 wt % 以下である請求項 3 に記載の固体高分子型燃料電池用電解質膜電極接合体。

## 【請求項 5】

前記一対の電極は、水素を含む燃料ガスが供給される燃料極と、酸素を含む酸化剤ガスが供給される酸素極と、からなり、

該酸素極に前記過酸化物分解触媒が配置される請求項 1 に記載の固体高分子型燃料電池用電解質膜電極接合体。

## 【請求項 6】

前記過酸化物分解触媒は、金属、金属酸化物、金属リン酸塩、金属フッ化物、大環状金属錯体から選ばれる一種以上である請求項 1 に記載の固体高分子型燃料電池用電解質膜電極接合体。

## 【請求項 7】

前記過酸化物分解触媒は、Ru、Ag、RuO<sub>2</sub>、WO<sub>3</sub>、CeO<sub>2</sub>、Fe<sub>3</sub>O<sub>4</sub>、CePO<sub>4</sub>、CrPO<sub>4</sub>、AlPO<sub>4</sub>、FePO<sub>4</sub>、CeF<sub>3</sub>、FeF<sub>3</sub>、Fe-ポルフィリン、Co-ポルフィリン、ヘム、カタラーゼから選ばれる一種以上である請求項 1 に記載の固体高分子型燃料電池用電解質膜電極接合体。

## 【請求項 8】

請求項 1 に記載の固体高分子型燃料電池用電解質膜電極接合体を備えた固体高分子型燃料電池。

## 【発明の詳細な説明】

## 【技術分野】

## 【0001】

本発明は、固体高分子型燃料電池に関し、特に固体高分子型燃料電池に用いられる電解質膜電極接合体に関する。

## 【背景技術】

## 【0002】

ガスの電気化学反応により電気を発生させる燃料電池は、発電効率が高く、排出されるガスがクリーンで環境に対する影響が極めて少ない。そのため、近年、発電用、低公害の自動車用電源等、種々の用途が期待されている。

## 【0003】

なかでも、固体高分子型燃料電池は、80℃程度の低温で作動させることができ、大きな出力密度を有する。固体高分子型燃料電池は、通常、プロトン導電性のある高分子膜を電解質とする。電解質となる高分子膜（電解質膜）の両側にそれぞれ燃料極、酸素極となる一対の電極が設けられ電解質膜電極接合体（MEA）が構成される。この電解質膜電極接合体をセパレータで挟持した単セルが発電単位となる。そして、水素や炭化水素等の燃料ガスを燃料極に、酸素や空気等の酸化剤ガスを酸素極にそれぞれ供給し、ガスと電解質

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と電極との三相界面における電気化学反応により発電を行う。

【0004】

しかし、固体高分子型燃料電池は、長期間の運転により、電池性能が低下してしまうという問題を有する。電池性能の低下の原因としては、例えば、電解質膜や電極の劣化が挙げられる。固体高分子型燃料電池の運転時には、酸素極において、水素と酸素とから水が生成される。しかし、運転条件等によっては、酸素極における酸素の還元が2電子反応で止まってしまい、過酸化水素( $H_2O_2$ )が生成されることがある。生成された過酸化水素は、例えば、金属イオン等の存在下でラジカル分解する。その過酸化水素ラジカルにより、電解質膜や電極が損傷を受け劣化すると考えられる。

【0005】

また、電解質膜の多くは、炭化水素系材料あるいはフッ素系材料からなる高分子膜である。従来、フッ素系電解質膜は、過酸化水素等の過酸化物によりほとんど損傷を受けないと考えられてきた。しかし、種々検討を重ねた結果、フッ素系電解質膜であっても、過酸化物により損傷を受ける場合があるということがわかった。この場合、過酸化物によりC-F結合が分解されるため、フッ酸等が生じる問題がある。

【0006】

過酸化物による電解質膜等の劣化を抑制し、燃料電池の耐久性を向上させる試みとして、例えば、ルテニウム、マンガン、コバルト等の金属、若しくはそれらの酸化物等を、電解質膜や電極に含有させることが提案されている(例えば、特許文献1、2参照。)

【特許文献1】特開2001-118591号公報

【特許文献2】特開2003-123777号公報

【発明の開示】

【発明が解決しようとする課題】

【0007】

しかしながら、上記特許文献1、2に示された手法では、含有させる金属及びその酸化物として、資源量が少なく高価な金属を用いる。そのため、資源の確保、コストの面において、実用化には問題がある。また、過酸化物の分解効果を向上させるべく、上記金属や酸化物の含有量を増加させると、電池反応が阻害されてしまうという問題もある。さらにまた、固体高分子型燃料電池の運転時には、電池内部は80℃程度の高温度下、酸性雰囲気等の過酷な環境となる。このような高温かつ酸性の条件下では、含有させた金属や酸化物は溶出し易い。それ故、過酸化物の分解効果を持続させることは難しい。

【0008】

本発明は、このような実状に鑑みてなされたものであり、過酸化物を分解する過酸化物分解触媒を多量に用いることなく、電池内で生成された過酸化水素等の過酸化物を効率良く分解することができる固体高分子型燃料電池用電解質膜電極接合体を提供することを課題とする。また、その電解質膜電極接合体を用いることにより、長期間運転した場合でも、電池性能が低下し難い固体高分子型燃料電池を提供することを課題とする。

【課題を解決するための手段】

【0009】

本発明の固体高分子型燃料電池用電解質膜電極接合体は、イオン導電性を有する電解質膜と、該電解質膜の両側に設けられた一対の電極と、を備え、前記一対の電極の少なくとも一方に、過酸化物を分解する過酸化物分解触媒が濃度差をもって配置されることを特徴とする。

【0010】

本発明の電解質膜電極接合体では、電解質膜の両側にそれぞれ燃料極、酸素極となる一対の電極が配置される。この燃料極および酸素極の少なくとも一方に、過酸化物分解触媒が含まれる。

【0011】

電極において、過酸化物分解触媒は濃度差をもって配置される。ここで、「濃度差をもつ」とは、電極において過酸化物分解触媒の濃度は一定ではなく、電極の領域によって酸

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化物分解触媒の濃度が異なることを意味する。濃度差は、電極の厚さ方向にあってもよく、電極の面方向にあってもよい。

【0012】

例えば、過酸化化物分解触媒を、過酸化化物が多く生成すると予想される領域には、その濃度が高くなるよう配置し、そうでない領域には、その濃度が低くなるよう配置する。このように配置することで、過酸化化物分解触媒を増量することなく、効果的に過酸化化物を分解することができる。また、過酸化化物分解触媒を、電解質膜と電極との界面付近に、その濃度が高くなるよう配置すると、生成した過酸化化物の電解質膜への拡散を、効果的に抑制することができる。

【0013】

このように、本発明の電解質膜電極接合体では、電極に配置される過酸化化物分解触媒の濃度分布を調整することにより、過酸化化物の生成、拡散状態に応じて、過酸化化物を効率的に分解、無害化することができる。それ故、使用する過酸化化物分解触媒が少量であっても、電極および電解質膜の劣化抑制効果は高い。また、本発明の電解質膜電極接合体は、少量の過酸化化物分解触媒で、効率良く過酸化化物を分解することができるため、コスト面でも実用的である。

【0014】

本発明の固体高分子型燃料電池は、上記本発明の電解質膜電極接合体を備えることを特徴とする。すなわち、本発明の固体高分子型燃料電池では、運転時に過酸化化物が生成しても、過酸化化物は過酸化化物分解触媒により速やかに分解される。そのため、運転時における電解質膜や電極の劣化が少なく、長期間運転した場合でも電池性能の低下は少ない。

【発明の効果】

【0015】

本発明の固体高分子型燃料電池用電解質膜電極接合体では、一対の電極の少なくとも一方に、過酸化化物を分解する過酸化化物分解触媒が濃度差をもって配置される。そのため、過酸化化物の生成、拡散状態に応じて、過酸化化物を効率的に分解、無害化することができる。したがって、本発明の電解質膜電極接合体を備えた固体高分子型燃料電池では、電極や電解質膜の劣化が少なく、長期間運転した場合でも電池性能の低下は少ない。

【発明を実施するための最良の形態】

【0016】

以下に、本発明の固体高分子型燃料電池用電解質膜電極接合体および固体高分子型燃料電池の実施形態を説明する。なお、本発明の固体高分子型燃料電池用電解質膜電極接合体および固体高分子型燃料電池は、下記の実施形態に限定されるものではない。本発明の固体高分子型燃料電池用電解質膜電極接合体および固体高分子型燃料電池は、本発明の要旨を逸脱しない範囲において、当業者が行い得る変更、改良等を施した種々の形態にて実施することができる。

【0017】

〈固体高分子型燃料電池用電解質膜電極接合体〉

本発明の電解質膜電極接合体は、イオン導電性を有する電解質膜と、該電解質膜の両側に設けられた一対の電極と、を備え、前記一対の電極の少なくとも一方に、過酸化化物を分解する過酸化化物分解触媒が濃度差をもって配置される。

【0018】

一般に、一対の電極、つまり、燃料極および酸素極は、それぞれ触媒層と拡散層とから構成される。触媒層は、電気化学反応の反応場であり、カーボンに担持された白金等の電極触媒と高分子電解質とを含む。拡散層は、触媒層への反応ガスの供給と、触媒層との間で電子の授受を行う役割を果たし、カーボクロス等の多孔質材料からなる。電解質膜の両表面には、それぞれ各電極の触媒層が形成され、各々の触媒層の表面には、拡散層が積層される。

【0019】

この場合、過酸化化物分解触媒は、電極を構成する触媒層に配置されることが望ましい。

過酸化物分解触媒を触媒層に配置することで、生成した過酸化物を速やかに分解することができるに加え、隣接する電解質膜への過酸化物の拡散も効果的に抑制することができる。

#### 【0020】

また、過酸化物分解触媒は、燃料極および酸素極のいずれか一方に配置されていてもよく、あるいは両方に配置されていてもよい。特に、生成した過酸化物を速やかに分解するという観点から、過酸化物分解触媒を酸素極に配置することが望ましい。

#### 【0021】

過酸化物分解触媒は、電極において濃度差をもって配置される。濃度差は、電極の厚さ方向にあってもよく、電極の面方向にあってもよい。濃度差の付け方は、特に限定されるものではなく、過酸化物の生成、拡散状態に応じて、適宜調整すればよい。例えば、電極の厚さ方向あるいは面方向において、濃度が段階的に変化するよう、濃度差を階段状につけてもよく、濃度が略連続的に変化するような濃度勾配をもたせてもよい。また、ある領域にのみ過酸化物分解触媒を配置して、過酸化物分解触媒を配置しない他の領域との濃度差をつけてもよい。

#### 【0022】

なかでも、過酸化物分解触媒を電極の厚さ方向に濃度差をもって配置することが望ましい。この場合、電解質膜側に向かって濃度値が増加する態様がより望ましい。電極の電解質膜側に過酸化物分解触媒を多く配置することで、電解質膜への過酸化物の拡散を、より効果的に抑制することができる。

#### 【0023】

また、上記態様において、電解質膜と電極との界面付近における過酸化物分解触媒の濃度は、過酸化物分解触媒の種類や、供給されるガスの加湿の程度にもよるが、1wt%以上であることが望ましい。1wt%未満の場合には、過酸化物の分解効果および電解質膜への拡散抑制効果が小さいからである。3wt%以上であるとより好適である。一方、電極における電気化学反応への影響を考慮すると、過酸化物分解触媒の濃度は、8wt%以下であることが望ましい。5wt%以下であるとより好適である。これら過酸化物分解触媒の濃度値は、過酸化物分解触媒を電極の触媒層に配置した場合には、触媒層の全体重量を100wt%とした場合の過酸化物分解触媒の重量割合である。

#### 【0024】

電極における過酸化物分解触媒の濃度差の有無は、例えば、電極をSIMS（二次イオン質量分析装置）により測定することで、あるいは、電極断面をEPMA（電子線マイクロアナリシス法）により測定することで、確認することができる。

#### 【0025】

過酸化物分解触媒は、過酸化物を分解する触媒作用を有するものであれば、特に限定されるものではない。例えば、金属、金属酸化物、金属リン酸塩、金属フッ化物、大環状金属錯体等が挙げられる。これらから選ばれる一種を単独で用いるか、あるいは二種以上を併用すればよい。なかでも、金属としてはRu、Ag等、金属酸化物としてはRuO<sub>2</sub>、WO<sub>3</sub>、CeO<sub>2</sub>、Fe<sub>3</sub>O<sub>4</sub>等、金属リン酸塩としてはCePO<sub>4</sub>、CrPO<sub>4</sub>、AlPO<sub>4</sub>、FePO<sub>4</sub>等、金属フッ化物としてはCeF<sub>3</sub>、FeF<sub>3</sub>等、大環状金属錯体としてはフェーポルフィリン、コーポルフィリン、ヘム、カタラーゼ等が好適である。特に、過酸化物の分解性能が高いという理由から、RuO<sub>2</sub>、CePO<sub>4</sub>を用いるとよい。

#### 【0026】

本発明の電解質膜電極接合体の作製方法は、特に限定されるものではないが、例えば、以下の方法により簡便に作製することができる。

#### 【0027】

第一の方法は、触媒層を形成するための触媒インクに、過酸化物分解触媒を混合する方法である。まず、電極触媒と高分子電解質とを水やアルコール等の溶媒に分散させた触媒インクに、過酸化物分解触媒を適宜混合し、過酸化物分解触媒の濃度の異なる種々の触媒インクを調製する。次いで、調製した種々の触媒インクを、ドクターブレード法、スプレ

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一法、スピンコート法等により電解質膜の表面に重ね塗りし、厚さ方向に過酸化水素分解触媒濃度の異なる触媒層を、電解質膜表面に形成する。

【0028】

また、上記調製した種々の触媒インクを、P T F E製シートの表面に重ね塗りし、厚さ方向に過酸化水素分解触媒濃度の異なる触媒層を、該シート表面に形成する。次いで、シート表面に形成された触媒層を、電解質膜の表面にホットプレス等により圧着する。圧着後、シートを剥離して、厚さ方向に過酸化水素分解触媒濃度の異なる触媒層を、電解質膜表面に形成する。

【0029】

第二の方法は、触媒層形成用粉末に、過酸化水素分解触媒を混合する方法である。まず、電極触媒と高分子電解質とからなる触媒層形成用粉末に、過酸化水素分解触媒を適宜混合し、過酸化水素分解触媒の濃度の異なる種々の触媒層形成用粉末を調製する。次いで、調製した種々の触媒層形成用粉末を、金属製支持体に順次静電塗布し、あるいは、コロナ放電等により順次付着させ、厚さ方向に過酸化水素分解触媒濃度の異なる触媒層を、金属製支持体表面に形成する。次いで、金属製支持体表面に形成された触媒層を、電解質膜の表面にホットプレス等により圧着する。圧着後、金属製支持体を剥離して、厚さ方向に過酸化水素分解触媒濃度の異なる触媒層を、電解質膜表面に形成する。

【0030】

第三の方法は、加水分解処理、湿式通電処理、スパッタ法、C V D（化学気相成長法）等により、過酸化水素分解触媒を電極の触媒層に配置する方法である。例えば、過酸化水素分解触媒として、金属酸化物、金属リン酸塩、金属フッ化物を用いる場合、加水分解処理では、まず、過酸化水素分解触媒を構成する金属の塩を水に溶解した金属塩水溶液を、触媒層と接触させる。次いで、その触媒層に酸溶液を接触させて加水分解すればよい。なお、金属塩は、水への溶解度が高い塩として、硝酸塩、硫酸塩、塩化物等が好適である。また、過酸化水素分解触媒として、金属を用いる場合、該金属の塩を水に溶解した金属塩水溶液を、触媒層と接触させる。そして、その触媒層に過酸化水素、ヒドラジン、ビタミンC、蔗糖等の還元剤を接触させて、金属に還元すればよい。

【0031】

湿式通電処理では、電解質膜の表面に触媒層が形成された電解質膜電極接合体前駆体を電解用電極の少なくとも一方として、過酸化水素分解触媒を構成する金属の塩を含む所定の溶液中で通電することにより、該前駆体表面に過酸化水素分解触媒を析出させればよい。

【0032】

以上説明した方法等により、過酸化水素分解触媒を含む触媒層を電解質膜の表面に形成した後、拡散層となるカーボンクロス等を、両極それぞれの触媒層の表面にホットプレス等により圧着し、電解質膜電極接合体とすればよい。

【0033】

なお、本発明の電解質膜電極接合体では、電解質膜の種類は特に限定されるものではない。例えば、全フッ素系スルホン酸膜、全フッ素系ホスホン酸膜、全フッ素系カルボン酸膜、含フッ素炭化水素系グラフト膜、全炭化水素系グラフト膜、全芳香族膜等を用いることができる。また、P T F E、ポリイミド等の補強材を含む、機械的特性を強化した複合高分子膜を用いてもよい。特に、耐久性等を考慮した場合には、全フッ素系の高分子膜を用いることが望ましい。なかでも、電解質としての性能が高いという理由から、全フッ素系スルホン酸膜を用いることが望ましい。全フッ素系スルホン酸膜の一例として、「ナフイオン」（登録商標、デュポン社製）、「アシプレックス」（登録商標、旭化成株式会社製）、「フレミオン」（登録商標、旭硝子株式会社製）等が挙げられる。

【0034】

〈固体高分子型燃料電池〉

本発明の固体高分子型燃料電池は、上記本発明の電解質膜電極接合体を備える。例えば、本発明の電解質膜電極接合体を、セパレータを介して複数個積層させて構成すればよい。電解質膜電極接合体を挟持するセパレータとしては、集電性能が高く、酸化水蒸気雰囲気

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気下でも比較的安定な焼成カーボン、成形カーボンや、ステンレス材料の表面に貴金属や炭素材料を被覆したもの等を用いればよい。

#### 【実施例】

##### 【0035】

上記実施形態に基づいて、電極の触媒層に、厚さ方向に濃度差をもつよう過酸化物分解触媒を配置して、電解質膜電極接合体を作製した。作製した電解質膜電極接合体を用いて電池反応を行い、電解質膜および電極の劣化の程度を調査した。以下、順に説明する。

##### 【0036】

#### 〈電解質膜電極接合体の作製〉

##### (1) 実施例1の電解質膜電極接合体

過酸化物分解触媒として $\text{CePO}_4$ を用い、電解質膜電極接合体（以下、適宜「MEA」と称す。）を作製した。まず、 $\text{CePO}_4$ を含まない触媒インクを調製した。カーボンに担持された白金触媒（ $\text{Pt}/\text{C}$ 触媒、白金担持率60wt%）に、蒸留水、エタノール、プロピレングリコール、ナフィオン溶液（22wt%、デュポン社製）を加え、超音波ホモジナイザーで混合して、触媒インクとした。次いで、調製した触媒インクを、テフロン（登録商標、デュポン社製、以下同じ。）製のシート表面に、ドクターブレード法により塗布した。その後、室温で乾燥させて溶媒を除去し、シート表面に、過酸化物分解触媒を含まない過酸化物分解触媒非含有層を形成した。過酸化物分解触媒非含有層の厚さは、約10 $\mu\text{m}$ であった。

##### 【0037】

次に、上記触媒インクに、所定量の $\text{CePO}_4$ 粉末を混合し、 $\text{CePO}_4$ 濃度が1wt%、3wt%、5wt%となる3種類の触媒インクを調製した。これら3種類の触媒インクを、 $\text{CePO}_4$ 濃度の低い順に、上記過酸化物分解触媒非含有層の表面にスプレー塗布、乾燥させて、厚さ方向に $\text{CePO}_4$ 濃度の異なる過酸化物分解触媒含有層を形成した。触媒インクの塗布は、各々の濃度につき5回ずつ行い、合計15回行った。過酸化物分解触媒含有層の厚さは、約10 $\mu\text{m}$ であった。

##### 【0038】

過酸化物分解触媒非含有層と過酸化物分解触媒含有層とが形成された上記シートを、電解質膜（商品名「ナフィオン」、登録商標、デュポン社製、膜厚50 $\mu\text{m}$ 、以下同じ。）の一方の表面に、圧力約4.9MPa、温度約120℃でホットプレスした。その後、シートのみを剥離して、電解質膜の表面に、電解質膜側に向かって $\text{CePO}_4$ の濃度値が増加する触媒層を形成した。この電解質膜と触媒層との接合体を実施例1のMEAとした。なお、本実施例1のMEAにおいて、触媒層は、過酸化物分解触媒非含有層と過酸化物分解触媒含有層とから構成される。

##### 【0039】

##### (2) 実施例2の電解質膜電極接合体

過酸化物分解触媒として $\text{RuO}_2$ を用い、MEAを作製した。まず、実施例1のMEAの作製と同様にして、 $\text{RuO}_2$ を含まない触媒インクを調製した。調製した触媒インクを、テフロン製のシート表面に、塗布、乾燥して、シート表面に、過酸化物分解触媒を含まない過酸化物分解触媒非含有層を形成した。過酸化物分解触媒非含有層の厚さは、約10 $\mu\text{m}$ であった。

##### 【0040】

次に、過酸化物分解触媒非含有層の表面に、 $\text{Ru}$ 錯体（ $\text{Ru}(\text{NO})(\text{NO}_3)_3$ ）水溶液（ $\text{Ru}$ として0.05wt%）を滴下した。その後、0.1Mのリン酸水溶液中で加水分解し、蒸留水で洗浄した。これより、シート表面には、過酸化物分解触媒非含有層の表面近傍に $\text{RuO}_2$ が固定された触媒層が形成された。

##### 【0041】

この触媒層が形成されたシートを、電解質膜の一方の表面に、圧力約4.9MPa、温度約120℃でホットプレスした。その後、シートのみを剥離して、電解質膜の表面に、電解質膜との界面付近に $\text{RuO}_2$ を含む触媒層を形成した。この電解質膜と触媒層との接

合体を実施例 2 の M E A とした。なお、触媒層の断面を、E P M A により測定したところ、 $RuO_2$  は、触媒層と電解質膜との界面付近に固定されていることが確認された。

【0042】

### (3) 比較例の電解質膜電極接合体

実施例 1 の M E A の作製で調製した触媒インク ( $CePO_4$  濃度: 3 wt %) を用いて触媒層を形成した。すなわち、 $CePO_4$  濃度が 3 wt % の触媒インクを、テフロン製のシート表面にスプレー塗布、乾燥させて、厚さ方向に  $CePO_4$  濃度が一定の触媒層を形成した。触媒インクの塗布は 15 回行い、触媒層全体で添加された  $CePO_4$  量を、実施例 1 の M E A と同じとした。形成された触媒層の厚さは、約  $10\mu m$  であった。

【0043】

触媒層が形成された上記シートを、電解質膜の一方の表面に、圧力約  $4.9MPa$ 、温度約  $120^\circ C$  でホットプレスした。その後、シートのみを剥離して、電解質膜の表面に、一定の濃度で  $CePO_4$  が含まれる触媒層を形成した。この電解質膜と触媒層との接合体を比較例の M E A とした。

【0044】

### 〈電解質膜等の劣化調査〉

作製した各 M E A を、耐久試験用のセルに組み込んだ。すなわち、M E A の両側に、ガス流路が形成されたカーボン製のセパレータを配置して、それを S U S 製の支持体で保持した。そして、触媒層が形成された方の電極 (酸素極) に加湿した空気を、他方の電極 (燃料極) に加湿した水素をそれぞれ供給して、24 時間作動させた。空気および水素の加湿温度は  $90^\circ C$ 、流量は  $100ml/min$ 、セルの作動温度は  $90^\circ C$  とした。

【0045】

セル作動中に、酸素極および燃料極から排出された水を回収した。回収水中のフッ化物イオン ( $F^-$ ) 濃度を、イオンクロマト装置 P I A - 1000 (株式会社島津製作所製) にて測定し、フッ化物イオン溶出速度 ( $\mu g / (cm^2 \cdot hr)$ ) を求めた。フッ化物イオン溶出速度は、単位時間、単位電極面積あたりに溶出されたフッ化物イオン量であり、各電極からの回収水の量と、回収水中のフッ化物イオン濃度とから算出される。フッ化物イオン溶出速度は、電解質膜および電極の劣化の程度を示す指標となる。つまり、フッ化物イオン溶出速度が大きいほど、電解質膜等の劣化が進行していることを示す。

【0046】

図 1 に、各 M E A におけるフッ化物イオン溶出速度の測定結果を示す。図 1 に示すように、触媒層に過酸化物分解触媒の濃度差がある実施例 1、2 の M E A では、フッ化物イオン溶出速度は  $0.1\mu g / (cm^2 \cdot hr)$  以下と小さくなった。これに対して、過酸化物分解触媒の濃度差がない比較例の M E A では、フッ化物イオン溶出速度が  $0.15\mu g / (cm^2 \cdot hr)$  と大きくなった。特に、実施例 1 の M E A と比較例の M E A とを比較すると、同じ量の過酸化物分解触媒を使用しても、濃度差をつけて配置した実施例 1 の M E A の方が、電解質膜等の劣化抑制効果が高いことがわかる。また、実施例 2 の M E A のように、過酸化物分解触媒を、電極と電解質膜との界面付近に配置すると、電解質膜等の劣化抑制効果が高いことがわかる。

【0047】

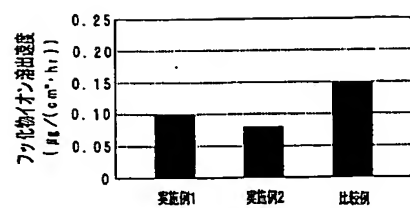
以上より、電極に過酸化物分解触媒が濃度差をもって配置された本発明の M E A では、電解質膜および電極の劣化が進行し難いことが確認できた。したがって、本発明の M E A を用いれば、長期間運転した場合でも電池性能の低下の少ない固体高分子型燃料電池を経済的に実現できる。

【図面の簡単な説明】

【0048】

【図 1】 実施例 1、2 および比較例の M E A におけるフッ化物イオン溶出速度の測定結果を示す。

【図 1】



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フロントページの続き

(72)発明者 森本 友

愛知県愛知郡長久手町大字長湫字横道4番地の1 株式会社豊田中央研究所内

(72)発明者 小林 雅史

愛知県豊田市トヨタ町1番地 トヨタ自動車株式会社内

(72)発明者 加藤 学

愛知県豊田市トヨタ町1番地 トヨタ自動車株式会社内

(72)発明者 竹内 仙光

愛知県豊田市トヨタ町1番地 トヨタ自動車株式会社内

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